

potential  $\varphi_\beta$  is omitted. Various refinements, such as variation of  $K$  and  $\gamma/d$  with  $z$  and  $\psi_0$  and a correction to the van der Waals energy due to the difference between the medium of the inner region and the particle medium, should not affect the general argument.

Part of the work by one of us (S. L.) was carried out at the National Research Council, Ottawa, Canada.

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### Permeation of Gaseous Oxygen through Vitreous Silica

THE permeation of gaseous oxygen through vitreous silica has been measured over the temperature-range 950°–1,080° C. in a permeation cell constructed with two portions separated by a thin-walled spherical bulb with a short neck. The bulb was 25 mm. outside diameter, and served as the membrane of vitreous silica; its area was 18.9 cm.<sup>2</sup> and thickness 0.27 mm. The thickness was determined from electrical capacitance measurements. The silica was used as blown; and no cleaning was done with hydrofluoric acid. The oxygen pressure, 300–800 mm. mercury, was applied to the convex side of the bulb. The low-pressure side led directly to a mass spectrometer with no leak intervening. The rate of permeation of gas was measured<sup>1</sup>, in this case by the peak height of mass 32. It was assured that true permeation, and not merely degassing, was being measured by: (1) observing the slow rise of the oxygen peak after application of oxygen to the high-pressure side, (2) attainment of steady-state flow and then, (3) slow decay of the peak after the gas was removed from the high-pressure side.

The experimental values of rate of permeation  $P$  on an Arrhenius-type plot of  $\log P$  against  $1/T$  yielded a good straight line, giving the results shown in Table 1. The units of  $P$  are those used by Barrer<sup>2</sup>; cm.<sup>3</sup> gas (S.T.P.) per sec. for 1 mm. thickness per cm.<sup>2</sup> area per cm. mercury difference of gas pressure.

Table 1

Temperature (° C.)	Rate of permeation $P$
900	$9.00 \times 10^{-13}$
950	$1.25 \times 10^{-12}$
1,000	$1.85 \times 10^{-12}$
1,050	$2.50 \times 10^{-12}$
1,100	$3.50 \times 10^{-12}$

From the slope of this plot an activation energy of permeation of 22,000 cal. per mole was derived.

The lag method of Daynes<sup>3</sup> and Barrer<sup>2</sup> is ideally adapted for the mass spectrometer to measure the rate of attainment of steady-state flow. By this method the diffusion constant  $D$ , in cm.<sup>2</sup>/sec., was found to be  $1.2 \times 10^{-8}$  at 1,078° C. and  $4.2 \times 10^{-9}$  at 950° C., yielding diffusion activation energy of 27,000 cal. for oxygen in vitreous silica. The lag time at 950° C. for the steady state was slightly more than 8 hr. in this particular cell with a wall 0.27 mm. thick.

The solubility was derived from the relationship  $S = 7.6 P/D$ , and found to be  $1.9 \times 10^{-3}$  at 1,078° C. and  $2.3 \times 10^{-3}$  at 950° C. The units are cm.<sup>3</sup> gas (S.T.P.) per cm.<sup>3</sup> solid for 76 cm. gas pressure applied.

The fact that molecular oxygen is the diffusing species is indicated by the observation that the rate of permeation was proportional to the first power of the pressure.

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### Aniline Oxidation Initiated by Ultrasonic Waves

IN order to explain the chemical processes occurring in the ultrasonic field, Lindström and Lamm<sup>1</sup> assumed that the principal reaction occurring during the ultrasonic treatment of water is its decomposition into radicals:



By means of this reaction it is possible to explain a number of chemical processes<sup>2-6</sup>, the oxidation of aniline included.

Aniline solutions (0.5, 1, 2 and 3 per cent, Merck) were used. All the solutions were prepared in redistilled water. The ultrasonic treatment was carried out in identical chemical vessels, containing 50 ml. of the desired aniline solution. A magnetostrictive transducer of 5.1 cm.<sup>2</sup> radiation area was cooled by air in such a manner that the initial solution temperature (17°–18° C.) rose only by 4°–7° C., in accordance with the duration of the ultrasonic treatment. All the solutions were treated with the waves of 21-ke./sec. frequency and electric power of about 4.5 W./ml. of the solution.

All the aniline solutions of the appropriate concentration were treated with ultrasonic waves during 2 min. In the course of the treatment minute oxygen bubbles were let through every solution (about 35–40 bubbles per min.). After the treatment the solutions were poured into small calibrated cylinders with ground-in stoppers.

In the course of the observations it was found that the aqueous aniline solutions form different oxidation products after treatment as shown in Table 1.

Table 1

Aniline solution concentration (per cent)	Ultrasonic treatment duration	Colour of dye
0.5	2 min.	violet
1.0	"	violet-blue
2.0	"	orange
3.0	"	black shot with green